(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 376 704 A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 89313623.4

(22) Date of filing: 27.12.89

(51) Int. Cl.5: C11D 3/39, C11D 1/29, C11D 1/75, C11D 1/83, C11D 3/36, C01B 15/037

(30) Priority: 28.12.88 GB 8830296

(43) Date of publication of application: 04.07.90 Bulletin 90/27

(84) Designated Contracting States: CH DE ES FR GB IT LI NL SE

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(54) Bleaching composition.

(57) Solutions of hydrogen peroxide which are alkaline, can be thickened with a combination of surfactant and electrolyte without unacceptable loss of stability. Surfactant may be alkyl ether sulphate:
$R(OC_2H_4)_nOSO_3M$
or a combination of amine oxide $R(CH_3)_2NO$ with alkane sulphonate RSO_3M or alcohol sulphate $ROSO_3M$ where any R is C_8 to C_{20} alkyl and any M is a solubilising cation and n is 0.5 to 5. Stabiliser is present and may be colloidal hydrous stannic oxide or may be a phosphonate as specified in EP-B-9839.

EP 0 376 704 A1

BLEACHING COMPOSITION

This invention relates to thickened liquid bleach compositions which may be suitable for sale and use as a domestic bleach. Pourable domestic bleach is frequently thickened by including one or more surfactants which, in the presence of electrolyte, act to thicken the solution rendering it more viscous than water. Thickening of a pourable domestic bleach helps the user to control dispensing of the composition and retards drainage from surfaces to which it is applied. This invention relates to such compositions which include surfactant and electrolyte to increase the viscosity. The compositions of the invention may be pourable or may be even more viscous so as not to be poured easily.

A domestic bleach needs to be adequately stable so that a substantial proportion of the bleaching agent survives during storage between manufacture and use. Prior to this invention commercial liquid bleach products have frequently utilised hypochlorite as bleaching agent.

It is well known that hydrogen peroxide is unstable unless stabilising agents are present. These counteract decomposition catalysed by transition metal ions. Hydrogen peroxide gives better bleaching action if used under alkaline conditions. However, stabilisation of hydrogen peroxide under alkaline conditions is difficult and in consequence commercial solutions of hydrogen peroxide have generally been acidic for the sake of stability. Certain phosphonates able to stabilise hydrogen peroxide in alkaline solution are disclosed in EP-B-9839 (Unilever).

The presence of electrolyte tends to cause decomposition of alkaline hydrogen peroxide solution. For instance, we have found that a 4% by weight solution of hydrogen peroxide, made alkaline to pH 10 and containing 0.25% of ethylene diamine tetramethylene phosphonic acid as stabiliser (which is not as effective as the phosphonates in accordance with EP-B-9839) was found to retain 95% of its hydrogen peroxide after two weeks storage at 37° C. By contrast, 85% or less of the hydrogen peroxide was retained if the solution also contained 1% by weight of sodium chloride, while only about 50% of the hydrogen peroxide was retained if the solution contained 10% by weight of sodium chloride. Similar results were observed using sodium tripolyphosphate rather than sodium chloride as the added electrolyte. Doubling the quantity of the phosphonate stabiliser had little effect on the rate of decomposition.

Thus, any attempt to make a surfactant-thickened, alkaline domestic liquid bleach product using hydrogen peroxide as the bleaching agent would encounter the potential problem that the thickening of the solution would require the presence of some electrolyte but that this electrolyte would serve to accelerate decomposition of the peroxide.

We have now found, however, that it is possible to formulate an aqueous alkaline solution of hydrogen peroxide which is thickened with surfactant and electrolyte yet does have sufficient stability to be useful as a commercial product.

According to the present invention there is provided a liquid bleaching composition comprising an aqueous alkaline solution containing hydrogen peroxide, a stabiliser therefor, electrolyte other than surfactant, and surfactant selected from:

a) an alkyl ether sulphate of the formula:

$R(OC_2H_4)_n\text{-}OSO_3M$

where R is an alkyl group containing 8 to 20 carbon atoms, n has an average value in the range 0.5 to 12, preferably 1 to 6, and M is a solubilising cation.

b) a combination of a nonionic or amphoteric surfactant and an anionic surfactant which is either a C_8 to C_{20} alkane sulphonate or a C_8 to C_{20} alcohol sulphate.

We have found that use of a surfactant as specified above is advantageous in achieving thickening with a fairly low electrolyte concentration. This may make it possible for the electrolyte to be provided by ions which are in the composition for other reasons, without deliberate addition of salt for the sole purpose of enhancing ionic strength. Apart from considerations of peroxide stability, a benefit of a low electrolyte concentration is a reduced tendency for the product to leave streaks on a surface which is cleaned with it.

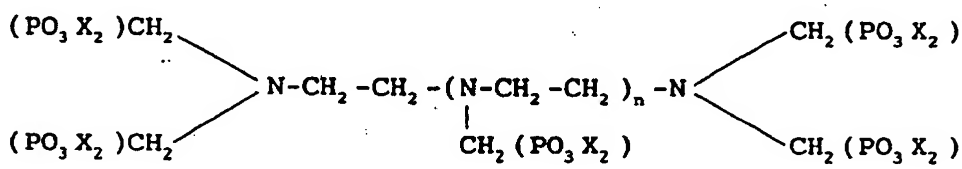
When the surfactant is a combination, in accordance with the alternative (b) above, a preferred possibility for the nonionic/amphoteric surfactant is an amine oxide surfactant, preferably a trialkyl amine oxide with one long chain alkyl of 8 to 20 carbon atoms and two alkyl groups of 1 to 4 carbon atoms. Then, if primary alcohol sulphate is the anionic surfactant the weight ratio of amine oxide:alcohol sulphate is preferably in the range from 82:18 to 65:35; better 80:20 to 65:35, even better 80:20 to 70:30.

Alkane sulphonate is preferred over alcohol sulphate because the viscosity is less sensitive to changes in the composition, so making it easier to produce an end product with repeatable viscosity. The weight ratio of amine oxide to alkane sulphonate (when this is used) is preferably in the range from 80:20 to 50:50 or better 65:35, and preferably in the narrower range from 70:30 to 65:35.

One or more further surfactants may also be included, within the scope of this invention. The total concentration of surfactant may lie in a range from 0.75 to 6% by weight based on the whole composition and may lie in the narrower range from 0.75 to 3%, especially if the composition is pourable. Concentrations above 6% by weight might be used but are less preferred.

The electrolyte concentration in a composition of this invention may be such that the total amount of salts other than surfactant is not more than 7% by weight, better not more than 5% or 3%. The electrolyte level may be such as to give a concentration of electrolyte in the range 0.05 to 0.30 molar, preferably 0.1 to 0.2 molar. Once again higher concentrations may be used but are less preferred.

Stabiliser for the hydrogen peroxide may be a phosphonate sequestrant in accordance with EP-B-9839, which defines the phosphonate compounds as of the general formula:



wherein n = 1-4; and X is H or a water-soluble cation selected from the group consisting of alkali metals, ammonium, substituted ammonium and alkaline earth metals. Such a sequestering agent may be used in an amount from 0.01 to 1% by weight. This is approximately 1.5×10^{-4} to 2×10^{-2} molar.

These compounds are effective to counter decomposition catalysed by iron but are less effective against manganese. We have found that it may be possible to prevent contamination by traces of manganese (e.g. by use of sufficiently pure raw materials) so that a separate stabiliser against manganese may not be required. However, if required a separate stabilising agent to counteract manganese may be a phosphate salt used in an amount from 0.5% up to 4% by weight, preferably 1 to 3% (reckoned as anhydrous salt). Tetrasodium pyrophosphate may be used as such a salt.

Another possible stabilising agent which we have found to be effective in alkaline solution against decomposition caused by transition metals including both iron and manganese, is colloidal hydrous stannic oxide.

This stabilising agent is preferably formed in-situ in the solution as the product of hydrolysis of a soluble tin compound. Various tin compounds can be added to the solution to undergo hydrolysis to form the stannic oxide, including tin sulphate, sodium stannate, tin dichloride and tin tetrachloride.

Suitable concentrations of tin compound in the composition may lie in the range from 10^{-4} molar to 10^{-2} molar, preferably 3×10^{-3} to 6×10^{-3} molar. The quantity of tin compound should not be substantially greater than necessary, since excess of it can itself cause peroxide decomposition. An optimum concentration of the tin compound (or any stabiliser) can be determined by making test solutions with various concentrations of the stabiliser and analytically determining the amount of hydrogen peroxide remaining after a period of storage.

An appropriate viscosity for a pourable composition having the appearance of a thick liquid is a dynamic viscosity in the range from 40 to 250 centipoise (0.05 to 0.25 Pa.sec), preferably about 100 centipoise (0.1 Pa.sec). More viscous liquids for example with viscosity in the range from 250 to 1000 centipoise or more are also within the scope of the invention.

Since the compositions of this invention are generally aqueous, they will usually have specific gravity close to unity. Consequently values of kinematic viscosities (in stokes) will be numerically approximately the same as values of dynamic viscosity (in poise). Dynamic viscosities expressed in Pascal.sec will be approximately 1000 times kinetic viscosities expressed in $m^2.sec^{-1}$.

The pH of the solution is preferably in the range from 8.0 to 10.5, better 8.5 to 9.8 or 10.0. With a phosphonate stabiliser it is further preferred that the pH is in the narrower range from 9.2 to 9.8, while with colloidal stannic oxide as stabiliser it is preferable to use a slightly lower pH in the range from 8.7 to 9.3. A buffer may be included to maintain pH at the desired value, but this may not be necessary. A phosphate, if present, will give a buffering action. Another compound which may be used for this purpose is borax.

The concentration of hydrogen peroxide in compositions of this invention, reckoned as pure H_2O_2, desirably lies in the range from 1 to 15% by weight preferably 2 to 10% by weight.

Example 1

Formulations were prepared containing the constituents set out in Table 1 below. The compositions were stored in plastic bottles at 37° C. At intervals aliquots were removed and titrated with potassium permanganate to determine the level of hydrogen peroxide remaining. Results are included in Table 1.

The viscosity of these formulations was measured using a Ubbelohde capillary viscometer and found to be approximately 100cS.

Table 1

Constituent	% by weight		
	A	B	C
Hydrogen peroxide (reckoned as anhydrous)	5	5	5
Tallow dimethylamine oxide	1.0	1.0	1.0
Sodium alkane sulphonate	0.5	0.5	0.5
Perfume	1.0	1.0	1.0
Tetrasodium pyrophosphate (reckoned as anhydrous)	1.8	-	-
Phosphonate stabiliser according to EP 9839	0.15	-	-
Borax (reckoned as anhydrous)	-	1.6	1.6
Sodium stannate trihydrate	-	0.5	0.1
Sodium hydroxide to give:	pH 9.6	pH 9.6	pH 9.0
Water	---- balance to 100% -----		
H_2O_2 remaining after 50 days:	85%	79%	
H_2O_2 remaining after 100 days:			96%

Example 2

The procedure of Example 1 was repeated, using formulations with the same amounts of hydrogen peroxide, surfactant, perfume and dye. Various tin compounds were used at a concentration of 6 x 10^{-3} molar, both with and without 3.0% borax decahydrate. Glass bottles were used, which are somewhat detrimental to stability. In every case pH was 9.6 initially. Proportions of hydrogen peroxide remaining after 28 days were:-

$SnCl_2$ with borax	68%
Na_2SnO_3 with borax	47%
$SnSO_4$ with borax	45%
Na_2SnO_3 without borax	96%
$SnCl_4$ without borax	68%

Example 3

A range of formulations were prepared, all containing:

Hydrogen peroxide	5.0% reckoned as anhydrous
Tetrasodium pyrophosphate decahydrate	3.0% (approx 1.8% reckoned as anhydrous)
Phosphonate stabiliser according to EP 9839	0.3%
Perfume	0.1%
Sodium hydroxide	to pH 9.6
Thickening system	variable
Water	--- balance to 100% ---

The thickening systems used various constituents and varied both in the properties and total amounts of materials employed.

The thickening systems contained tallow dimethylamine oxide (AO) together with sodium lauryl sulphate (SLS), or sodium alkane sulphonate (SAS), which was a secondary alkane sulphonate derived from an n-alkane mixture which is principally C_{13} to C_{18}.

Viscosities of the formulations were measured using a Ubbelohde capillary viscometer. The results obtained are shown in the accompanying Figures.

Figure 1 shows variation in viscosity with the proportion of SLS in an AO/SLS mixture, while the total amount of AO plus SLS is varied from 1.1% to 1.9% by weight of the composition.

Figure 2 shows variation in viscosity for AO/SAS mixtures while the total of AO plus SAS is varied from 1.2% to 2.6% of the composition. It can be seen that the viscosity maxima are broader peaks, while the maximum viscosity is less sensitive to variation in the total amount of AO plus SAS. For instance in Figure 1 the concentration of surfactant to give a viscosity of 100cS is 1.2%, and an increase from this of 0.2%, up to 1.4%, would double the viscosity to 200cS. In Figure 2 1.4% total surfactant gives a viscosity of 100cS. Increasing by 0.2% increases the viscosity to 150cS and a larger increase, to 1.8%, is required to achieve 200cS.

Example 4

A number of formulations were prepared using as surfactant a linear alkyl ether sulphate of general formula:

$R(OC_2H_4)_nOSO_3\ Na$

where the alkyl group R was C_{12} and C_{13} linear alkyl groups, and n had an average value of 3. Some of these formulations included a phosphonate stabiliser according to EP 9838. Others used stannous chloride which hydrolysed in-situ to colloidal hydrous stannic oxide. Peroxide stability was monitored, as in Example 1. Viscosities were determined using a Haake RV2 roto-viscometer at a shear rate of $21sec^{-1}$ which is appropriate for determining viscosities of pourable domestic bleach products. The formulations were as follows:

Constituent	% by weight	
Hydrogen peroxide (reckoned as anhydrous)	5	5
Alkyl ether sulphate	variable	
Sodium chloride		
Perfume	0.08	0.08
Sodium hydroxide to give:	pH 9.6	pH 9.6
Water	-- balance to 100% --	
H_2O_2 remaining after 5 weeks at 37°C	80%	79%

The amounts of alkyl ether sulphate and sodium chloride in various formulation, together with the results observed, are set out in the following Table.

Alkyl ether sulphate	3%	3%	3%	1.25%	1.25%
Sodium chloride	4%	5.5%	7%	6.5%	6.5%
Phosphonate stabiliser according to EP 9839	0.15%	0.15%	0.15%	0.15%	-
Stannous chloride dihydrate	-	-	-	-	0.14%
H_2O_2 remaining after 5 weeks at 37° C	75%	72%	71%	79%	80%
Viscosity (cP)	15	200	600	100	100

Example 5

Alkaline solutions of hydrogen peroxide were prepared containing surfactant, sodium chloride and stannic chloride which hydrolysed to colloidal hydrous stannic oxide.

Two surfactant combinations were used. The quantities of surfactant and sodium chloride were such as to give viscosities well in excess of that preferred for a pourable "thick liquid" type of bleach product. Smaller quantities could be used to give a "thick liquid" type of bleach product.

In each case the initial concentration of hydrogen peroxide, reckoned as anhydrous, was 4% by weight. The solutions were made alkaline to pH 10 with sodium hydroxide.

Stannic chloride was used at a concentration of 2.3×10^{-3} molar.

One surfactant system consisted of 4.5% by weight of C_{12}-C_{14} alkyl dimethyl amine oxide and 4.5% by weight sodium lauryl sulphate. This was used with a sodium chloride concentration of 9% by weight.

The second surfactant system consisted of 5% by weight of C_{11}-C_{15} secondary alcohol ethoxylated with average 3 ethylene oxide residues, and 5% by weight of sodium lauryl sulphate. This combination was used with 3.37% by weight sodium chloride.

The solutions were stored at 40° C and the amount of hydrogen peroxide remaining was determined at intervals. It was found that the amounts of hydrogen peroxide remaining were between 80 and 85% with either of the surfactant combinations.

Claims

1. A liquid bleaching composition comprising an aqueous alkaline solution containing hydrogen

peroxide, a stabiliser therefor, electrolyte other than surfactant, and surfactant selected from:

a) an alkyl ether sulphate of the formula:

$R(OC_2H_4)_nOSO_3M$

where R is an alkyl group containing 8 to 20 carbon atoms, n has an average value in the range from 0.5 to 12 and M is a solubilising cation.

b) a combination of a nonionic or amphoteric surfactant and an anionic surfactant which is either a C_8 to C_{20} alkane sulphonate or a C_8 to C_{20} alcohol sulphate.

2. A composition according to claim 1 wherein the surfactant is a combination of (i) a trialkyl amine oxide having one C_8 to C_{20} alkyl group and two C_1 to C_4 alkyl groups and (ii) a said anionic surfactant.

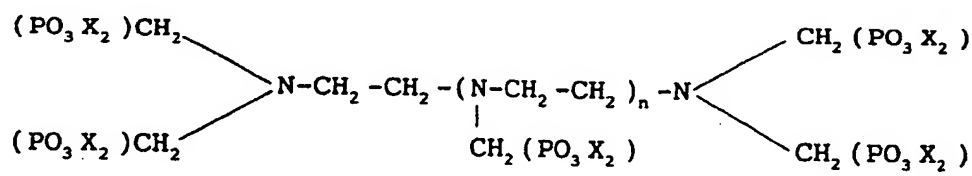
3. A composition according to claim 1 or claim 2 wherein the amount of electrolyte in solution is such that the total quantity of salts other than surfactant in the composition does not exceed 5% by weight based on the whole composition.

4. A composition according to claim 1 wherein the surfactant is a said alkyl ether sulphate and the electrolyte concentration is in the range from 0.75 to 10% by weight.

5. A composition according to any one of the preceding claims wherein the amount of surfactant present is in the range from 0.75 to 3% by weight based on the whole composition.

6. A composition according to any one of claims 1 to 5 wherein the stabiliser is colloidal hydrous stannic oxide.

7. A composition according to any one of claims 1 to 5 wherein the stabiliser is a compound of the formula:



wherein n = 1-4; and X is H or a water-soluble cation selected from the group consisting of alkali metals, ammonium, substituted ammonium and alkaline earth metals.

8. A composition according to any one of the preceding claims wherein the concentration of hydrogen peroxide, reckoned as pure H_2O_2, lies in the range from 1 to 15% by weight of the composition.

9. A composition according to any one of the preceding claims having a pH in the range from 8.5 to 10.

Fig. 1. VISCOSITY OF AO/SLS SYSTEM AS A FUNCTION OF ACTIVE LEVEL AND SLS CONTENT

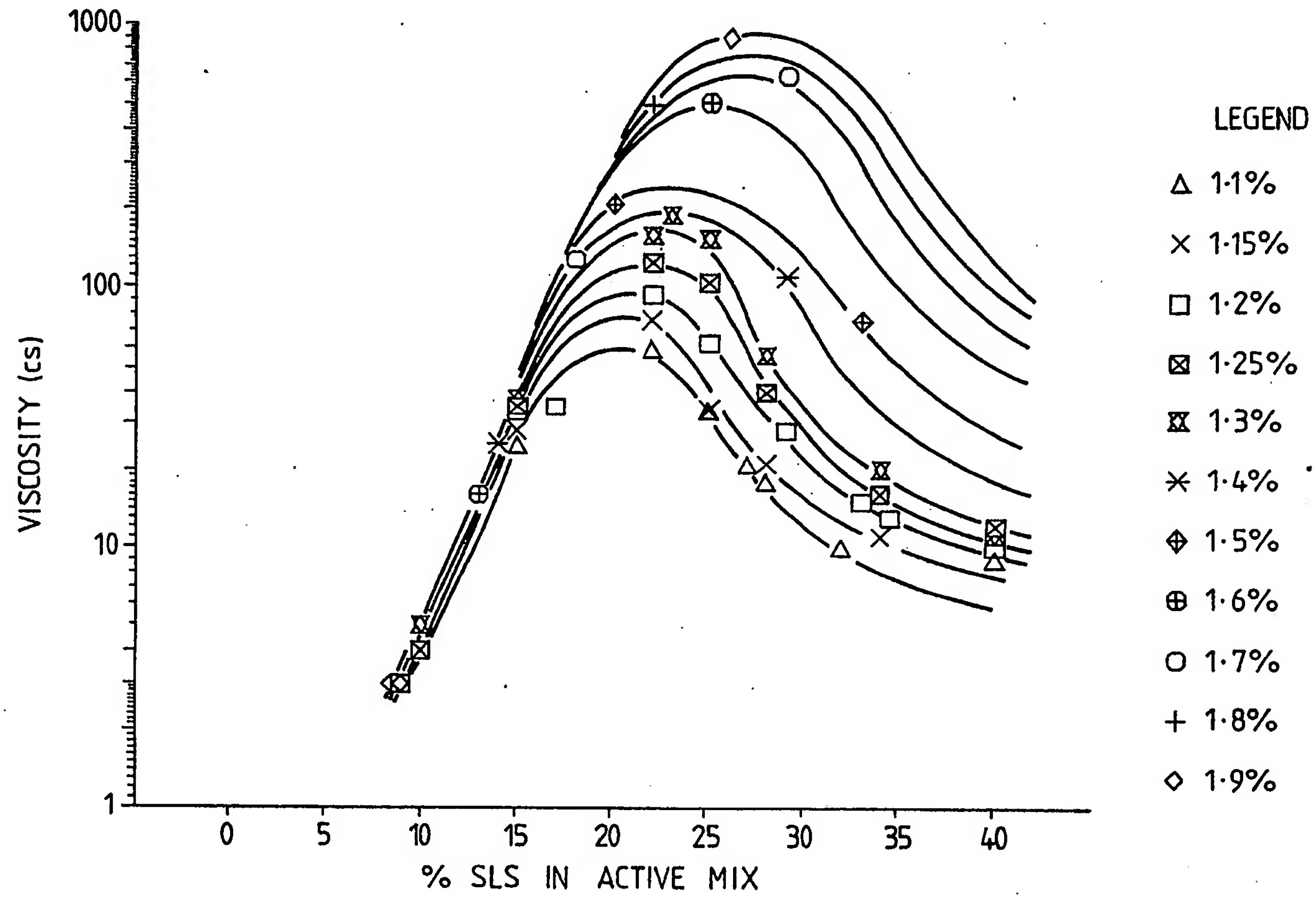
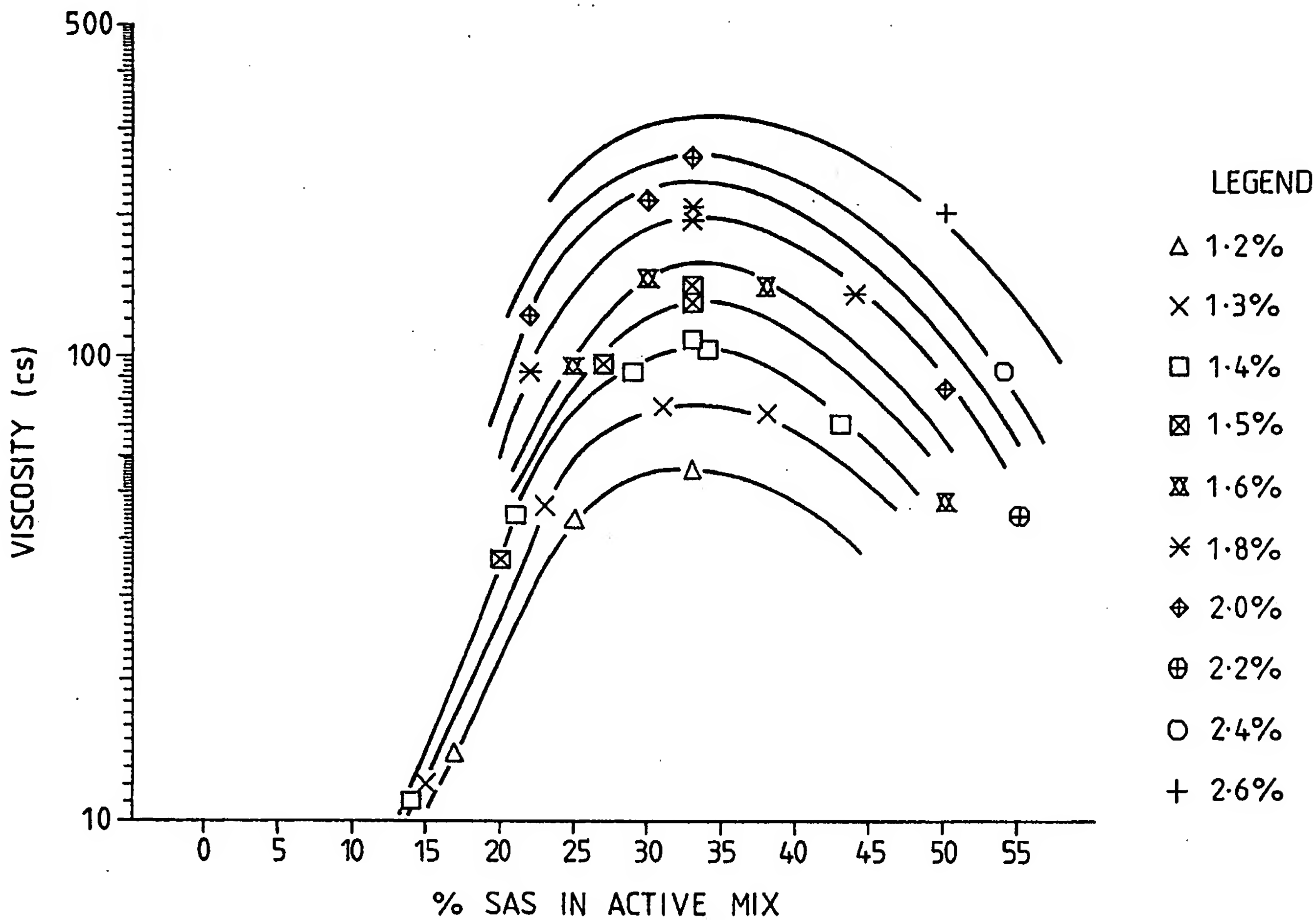


Fig. 2. VISCOSITY OF AO/SAS SYSTEM AS A FUNCTION OF ACTIVE LEVEL AND SAS CONTENT



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EUROPEAN SEARCH REPORT

Application Number

EP 89 31 3623

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	GB-A- 855 679 (UNILEVER LTD.) * whole document * ---	1,4,5,8	C 11 D 3/39 C 11 D 1/29 C 11 D 1/75 C 11 D 1/83 C 11 D 3/36 C 01 B 15/037
X	FR-A-2 140 822 (L'AIR LIQUIDE) * page 3, lines 1-34; claims 1,2,5,6,9-11 * ---	1,8,9	
Y	EP-A-0 037 184 (INTEROX CHEMICAL LTD.) * abstract; page 5,line 34-37; page 8, lines 10-14; page 10, lines 10-14; page 11, lines 23-31; page 13, lines 23-30; page 13, lines 23-30; page 15, lines 35-38; page 16, lines 1-3; claims 1-3,5,7,12-15,20,28,29 *	1,8	
A	---	3-5,7,9	
Y	US-A-3 388 069 (K. LINDNER et al.) * claims 1-10; column 3, lines 54-74 *	1,8	
A	---	2	
Y	CHEMICAL ABSTRACTS vol. 99, no. 22, 28 November 1983, page 113, column 2, abstract no. 177871e, Columbus, Ohio, US; & JP - A - 83 38800 (MITSUBISHI GAS CHEMICAL CO) 07-03-1983 * abstract *	1,8	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	idem ---	6	C 11 D
A	EP-A-0 087 049 (HENKEL KG) * claims * ---	1	
A	EP-A-0 141 759 (ATOCHEM) * abstract; claims * -----	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	16-03-1990	PELLI-WABLAT B

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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T : theory or principle underlying the invention
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